REMARKS

The Applicants gratefully acknowledge the Examiner's allowance of claims 12-14 and 16-21 and indication of allowable subject matter of claim 15.

The Examiner is thanked for his careful review of the claims. Claims 9, 10, 15, 23, and 24 have been amended to correct the typographical error identified by the Examiner. Claim 6 has been amended to correct a typographical error such that the metal contact region cleaning method of that claim is properly recited with antecedent basis. The Specification has been amended at the paragraphs of p. 16, lines 15-19, and p. 23, lines 10-20 also to correct typographical errors.

<u>Claim Rejections:</u>

Claims 1-6 are directed to a method for etching oxide on a semiconductor substrate. In the method, the oxide on the substrate is exposed to hydrofluoric acid vapor and water vapor in a process chamber that is held at temperature and pressure conditions which are controlled to form on the substrate no more than a sub-monolayer of etch reactants and etch products produced by the vapor as the oxide is etched by the vapor. This etching technique can also be applied to contaminant cleaning (claim 4), etch residue removal (claim 5), and metal contact region cleaning (claim 6).

Claims 1-6 were rejected under 35 U.S.C. §103(a) as being unpatentable over U.S. Patent No. 5,288,333, to Tanaka et al. The Examiner suggested that Tanaka's method of cleaning wafers using HF and water vapor would form no more than a sub-monolayer of reactants and products on a wafer being cleaned because Tanaka's method involves etching with HF and H_2O vapors. The Examiner further suggested that any reaction products

formed on the surface of a semiconductor device by Tanaka's method would be vaporized.

Tanaka suggests that his wafer cleaning process, also said to be employable as an oxide etch process, has a particular benefit of "avoiding formation of colloidal silica at and adjacent the gas/liquid and gas/solid interfaces," (Col. 2, lines 32-34). But in contradiction with the claimed sub-monolayer etching and cleaning methods of claims 1-6, Tanaka explicitly teaches the formation of a <u>liquid</u>, i.e., a condensed, interface during his etch/cleaning process, as explained below. The sub-monolayer reactant and product condition required by the claims precludes Tanaka's condensed interface.

To prevent formation of colloidal silica on a wafer during an etch/cleaning process, Tanaka prescribes "to allow no aerosol (mist) to exit in the atmosphere for the cleaning process" and "not to supply an aerosol to the silicon wafer and not to allow the cleaning vapor supplied to the silicon wafer to liquefy and form an aerosol," (Col. 5, lines 59-65). Tanaka prescribes that in the etch/cleaning chamber, vapor is "maintained at a temperature above its dew point to prevent the vapor from liquefying into an aerosol, [i.e., forming a mist,] within the dry cleaning chamber," (Col. 9, lines 53-56).

Tanaka describes an experimental vapor HF/H_2O etch process carried out under his non-aerosol conditions. In the experiment, a thermal oxide-coated silicon wafer was exposed to a vapor HF/H_2O mixture. Tanaka observed that "water was formed in the course of this reaction. As shown in Fig. 8, the water thus formed <u>collects as droplets</u> at the boundary between bare silicon and thermal oxidation, which move upward with progress of the etching," (Col. 18, line 67-Col. 19, line 4). Tanaka noted that when organic

contamination was present on the oxide and/or when the etch progressed in various directions, oxide islands were formed by the etch and the water droplets remained on boundaries between the oxide islands and the bare silicon, with colloidal silica forming around the droplets (Col. 19, lines 5-19).

To suppress this colloidal silica formation, Tanaka prescribes spinning of a wafer during the etch to uniformly distribute the etch vapor, and employing an ultraviolet radiation/ozone treatment to remove organic contamination (Col. 19, lines 20-46). Tanaka explains that "this process prevents droplets <u>from remaining</u> in island forms on the bare silicon surface owing to organic contamination, thereby eliminating the possibility of formation of colloidal silica in the etching and cleaning treatments," (Col. 19, lines 56-60).

Tanaka does not assert that water droplets are not formed by his non-aerosol vapor etch process; he asserts that the water droplets which are formed will not remain on the wafer if organic contamination is eliminated from the wafer and if the wafer is spun during the etch. Tanaka's efforts to inhibit formation of an aerosol mist do not inhibit water droplet formation; water condenses on the wafer even though a mist is not formed in the process chamber. Thus, Tanaka's vapor etch process conditions result in etch products that condense to form condensed droplets on the wafer surface. Once formed, the condensed droplets are found to remain on the surface if contamination is present and/or the etch is not uniform, and to be released from the surface if the etch proceeds uniformly and contamination is not present.

Tanaka's cleaning/etch conditions thus do not meet the requirement of claims 1-6 that no more than a sub-monolayer of etch reactants <u>and products</u>

be formed on a substrate; in Tanaka's process, full condensation of an etch product into liquid water droplets occurs. This condition is precluded by the sub-monolayer formation requirement of the claims.

It is apparent that Tanaka recognized this condensation limitation of his cleaning/etch process in that he suggests the use of a secondary wet cleaning step, as was conventionally understood to be required, to fully clean a wafer after a vapor cleaning/etch step. Specifically, Tanaka describes a wet cleaning process in which pure water and a cleaning chemical are sprayed on the wafer (Col. 17). Tanaka asserts that by employing a combination of vapor and wet processes, "excellent etching results are obtained with no particles remaining on the wafer," (Col. 17, lines 47-48).

In great contrast, the sub-monolayer etch and cleaning processes of the invention eliminate the need for a secondary wet clean process. As described in the instant Specification, the invention provides a vacuum cluster tool for metal line etching and cleaning, as well as metal via etching, cleaning, and metal deposition all carried out in the vapor regime, without the need for any liquid processing (pp. 42-44). For example, in a metal etch and deposition process provided by the invention, once a deposited metal layer is patterned, a sub-monolayer etch regime cleaning step in accordance with the invention is carried out, and thereafter, the wafer is immediately transferred to an interlayer dielectric deposition chamber for deposition of an interlayer dielectric over the patterned metal layer (p. 44, lines 1-10). No liquid cleaning or rinse step is required after the vapor clean/etch step.

This highly efficient process that eliminates a post etch wet clean was not previously thought to be effective, as evidenced by Tanaka's teaching. The sub-monolayer conditions provided by the invention are discovered,

however, to eliminate the need for the post wet clean while enhancing the results of the vapor etch process itself.

Based on this analysis, it is found that the conditions of Tanaka's HF/H_2O cleaning/etch process result in condensation of etch products on a silicon wafer being processed. The claims explicitly require an opposing condition, namely, that no more than a sub-monolayer of reactants and products be formed. This condition eliminates the water droplet formation of Tanaka's process and eliminates the need for Tanaka's secondary wet clean process.

The Examiner suggested that the term "sub-monolayer" of the claims is broad in its scope and thus does not further limit the claims in a way that would define the claimed invention over that of Tanaka. The Applicants respectfully submit that the instant Specification provides explicit description and figure representation of a "sub-monolayer" condition, and provides experimental evidence for clearly identifying a "sub-monolayer" condition over other possible vapor etching and cleaning conditions. The "sub-monolayer" limitation of the claims is therefore a fully defined requirement of the claims that is extensively explained by the Specification.

Specifically, pp. 15-16 and Figs. 2A-2D describe and depict four distinct operational HF vapor process regimes that are identified in accordance with the invention. The first regime, condensation, produces a liquid-phase layer of reactants and/or products. The second regime, multilayer processing, is produced by multiple layers of reactant and/or product species that are adsorbed in a manner that does not form a liquid on the substrate surface. The third regime, monolayer processing, results in a substantial coverage of the substrate surface by a single layer of adsorbed

reactant and/or product species. In the final, fourth regime, sub-monolayer processing, less than about 95% of a monolayer of reactant and/or product species are adsorbed on a substrate, and as with the multilayer and monolayer regimes, no condensation of liquid occurs at the substrate surface.

Examples 1-10 of the instant Specification provide explicit experimental evidence of distinctions between the four vapor processing regimes identified above. Further, the plots of Figs. 5 and 6 provide example etch rate data for various ranges of pressure and temperature that enable the identification of operation in a specific one of the processing regimes. The Specification goes on to describe characteristics of the sub-monolayer regime, e.g., explaining that for a given processing temperature, as reactant partial pressures are increased, the etch rate increases until monolayer conditions are approached; and that for given reactant partial pressures, as the process temperature is increased, the sub-monolayer etch rate also increases (pp. 20-21.)

Thus, in accordance with written description and enablement requirements, the instant Specification and figures fully describe and explain specific characteristics to be met for operation in the sub-monolayer regime of the invention. The claims' requirement of temperature and pressure control to form no more than a sub-monolayer of reactants and products correspond to the operational requirements set forth by the Specification, and thus do limit the claims.

The Examiner suggested that it would be obvious that no more than a sub-monolayer of etch reactants would be formed in Tanaka's method because Tanaka employed HF and H_2O vapor etching. As made clear by the discussion above, the use of vapor etching does not guarantee sub-monolayer

conditions. Vapor etching can result in condensed, multilayer, saturated monolayer, or sub-monolayer conditions. Tanaka's process results in the condensed conditions of his water droplet formation, leading to Tanaka's efforts to eliminate colloidal silica formation at the condensed water droplets. The invention requires sub-monolayer conditions, which eliminate the process difficulties encountered by Tanaka.

Accordingly, Tanaka does not teach, suggest, or hint at any technique for controlling pressure and temperature to form no more than a sub-monolayer of reactants and products on a substrate as required by the claims; Tanaka teaches techniques for removing colloidal silica produced in association with water droplets that condense during Tanaka's process. The Applicants therefore respectfully submit that the sub-monolayer processes of claims 1-6 are neither anticipated nor suggested by Tanaka.

Claims 7-11 and 22-24 were rejected under 35 U.S.C. §103(a) as being obvious over Rose, U.S. Patent No. 5,967,156.

Claim 7 is directed to a method of etching oxide on a semiconductor substrate. The method includes two steps. In one of the steps, the oxide on the substrate is exposed to a stream of frozen particles. In the other step, the oxide is exposed to hydrofluoric acid vapor and water vapor in a process chamber that is held at temperature and pressure conditions controlled to form on the substrate no more than a multilayer of etch reactants and etch products produced by the vapor as the oxide is etched by the vapor. This oxide etching method can also be employed for cleaning surface contaminants (claim 8).

Claims 22-24 all require that in a step of exposure of an oxide on a semiconductor substrate to a stream of frozen particles, the substrate temperature remain uncontrolled. These claims further require that the oxide layer further be exposed to hydrofluoric acid and water vapors under process temperature and pressure conditions that are controlled to form on the substrate no more than a multilayer of etch reactants and products as the oxide is etched by the vapor. Claim 23 requires this temperature and pressure control to form no more than a saturated monolayer of reactants and products; claim 24 requires this temperature and pressure control to form no more than a sub-monolayer of reactants and products.

Rose describes a technique for cleaning “foreign material” from a substrate surface by directing to the substrate a flow of reactant fluid 16 while simultaneously directing to the substrate an aerosol 21 of partially frozen particles 22, see Rose Fig. 1 and Col. 7, Lines 36-62. Referring also to Figs. 2-2C, Rose describes the function of his aerosol 21. Rose explains that reaction of a reactant fluid 16 (Fig. 1) with foreign material 10 on a substrate surface can result in non-volatile residue 20 (Figs. 1 and 2-2B) on the substrate surface, or can result in incorporation of a product compound 36 in the foreign material (Col. 8, lines 15-17).

The Examiner suggested that because Rose exposes oxide to frozen particles and etches the oxide with HF and water vapor, no more than a sub-monolayer of etch reactants would be formed by Rose's process. As explained above, this is not the case; no guarantee of a particular operational regime results from vapor processing. The use of HF and water vapor can result in condensed, multilayer, saturated monolayer, or sub-monolayer conditions. As explained in detail below, like Tanaka's process, Rose's process results in

condensed processing conditions, in contradiction with the requirements of the claims.

Rose teaches the simultaneous direction of reactant fluid 16 and aerosol 21 of particles 22 to a substrate region to be cleaned (Fig. 1) such that the aerosol particles remove the non-volatile product residues 20 that are found to result from the reaction between the reactant fluid and the foreign material on the substrate in Rose's cleaning process (Col. 8, lines 33-35).

As explained in the instant Specification at pp. 15-16, at the intersection of a very thick multilayer vapor process regime and a condensed regime, and in the condensed regime itself, etch and/or cleaning product residue is formed on a substrate. The instant Specification gives specific experimental examples and corresponding operational conditions that result in such residue. Claims 7-11 and 22-24 require the control of temperature and pressure such that this residue is not produced, i.e., require process conditions that result in no more than a multilayer formation and thus no residue formation. Rose does not meet this requirement because his process results in substrate surface residue, which is an indication of condensed regime operation.

Rose does not teach or even hint at techniques for controlling temperature and/or pressure conditions to reduce or eliminate process residue; instead, Rose relies on a simultaneous aerosol flow to dislodge and remove residue as it is produced on a substrate surface. The process of the invention eliminates Rose's need for the complicated operation of simultaneous and localized reactant flow and aerosol flow by instead controlling temperature and pressure to form no more than a multilayer of

reactants and/or products, and thus eliminates Rose's need for simultaneous reactant/aerosol flow.

Claims 22-24 require that while oxide on a substrate is exposed to a stream of frozen particles, the substrate temperature remain uncontrolled. In Rose's method, UV or IR light 40 (Fig. 1) 69 (Fig. 4) is directed to a reaction region to control temperature of the foreign material and the gases delivered to a wafer, and "to control the surface temperature of the wafer," (col. 10, lines 34-67; col. 11, lines 29-31). Rose therefore makes explicitly clear that control of temperature is to be carried out as a frozen aerosol is directed to a wafer. This is in direct contradiction to the requirement of claims 22-24 that the substrate temperature remain uncontrolled as the substrate is exposed to a stream of frozen particles. The Applicants accordingly respectfully submit that Rose simply provides no teaching or suggestion of the uncontrolled temperature conditions required by these claims.

Accordingly, the Applicants respectfully submit that Rose neither teaches nor suggests the processes of the invention of claims 7-11 and 22-24.

<u>Claim Objections:</u>

Claims 9, 10, 15, 23, and 24 were objected to because of a spelling error; the term "to from" in each of these claims was intended to read as "to form." Correction of this typographical error has been made in each of the identified claims.

The Applicants respectfully submit that all of the claims are now in condition for allowance, which action is requested. If the Examiner would

like to discuss this response, or to propose an Examiner's amendment, he is encouraged to telephone the undersigned Agent at his convenience.

Information Disclosure Statement:

Accompanying this reply is an Information Disclosure statement.-

Formal Drawings:

Accompanying this reply are 21 sheets of formal drawings.

Respectfully Submitted

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Marked-up Version of Amended Paragraph

P. 16, lines 15-19

Fig. 2D depicts the final operational regime, in which the vapor process parameters result in a condition whereby vapor-phase reactants 50 ~~from~~ form a sub-monolayer 62 on the surface of an oxide layer 54 to be etched on a silicon wafer 56. The sub-monolayer regime can be generally defined as one in which no more than about 95% of a monolayer exists.

Marked-Up Version of Amended Paragraph

P. 23, lines 10-20

The oxide etch characteristics of the multilayer regime were further investigated to provide identifying distinctions of this regime. There is shown in Fig. 7A a plot of oxide etch rate as a function of the partial pressure of water vapor, for a wafer temperature of 40° C, a total flow rate of 500 sccm, a total pressure of 250 T, and an HF vapor pressure of 7 T. These measurements were made on thermal oxide samples of about 5500 Å in thickness that were etched for several minutes while the thickness were measured using ellipsometry. The change in thickness per minute (etch rates) were computed from this data. From the plot it is seen that the multilayer regime is characterized by an oxide etch rate that is substantially linearly proportional to water vapor partial pressure.

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Marked-Up Amended Claims

6. A method for cleaning a metal contact region of a semiconductor substrate, comprising exposing the metal contact region to hydrofluoric acid vapor and water vapor in a process chamber held at temperature and pressure conditions that are controlled to form on the substrate no more than a sub-monolayer of reactants and products produced by the vapor as the ~~residue is removed~~ metal contact region is cleaned by the vapor.

9. The method of either of claims 7 or 8 wherein the process chamber temperature and pressure conditions are controlled to ~~from~~ form on the substrate no more than a saturated monolayer of etch reactants and products produced by the vapor as the oxide is etched by the vapor.

10. The method of either of claims 7 or 8 wherein the process chamber temperature and pressure conditions are controlled to ~~from~~ form on the substrate no more than a sub-monolayer of etch reactants and products produced by the vapor as the oxide is etched by the vapor.

15. The method of any of claims 12, 13, or 14 wherein the process chamber temperature and pressure conditions are controlled to ~~from~~ form on the substrate no more than a sub-monolayer of etch reactants and products produced by the vapor as the oxide is etched by the vapor.

23. The method of claim 22 wherein the process chamber temperature and pressure conditions are controlled to ~~from~~ form on the substrate no more than a saturated monolayer of etch reactants and products produced by the vapor as the oxide is etched by the vapor.

24. The method of claim 22 wherein the process chamber temperature and pressure conditions are controlled to ~~from~~ form on the substrate no more than a sub-monolayer of etch reactants and products produced by the vapor as the oxide is etched by the vapor.